

Claims

1. A phosphorus- and metal components-containing MFI-structured molecular sieve having a formula expressed in an anhydrous form and on the basis of oxide weight, as follows: (0~0.3) Na₂O (0.5~5.5) Al₂O₃ (1.3~10) P₂O₅ (0.7~15) M₁_xO_y (0.01~5) M₂_mO_n (70~97) SiO₂, wherein M₁ is one of metals selected from the group consisting of Fe, Co and Ni; x represents the atom number of M₁; y represents a number required by the oxidation state of M₁; M₂ is one selected from the group consisting of Zn, Mn, Ga and Sn; m represents the atom number of M₂; and n represents a number required by the oxidation state of M₂.
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2. The molecular sieve according to claim 1 having a formula expressed in an anhydrous form and on the basis of oxide weight as follows: (0~0.2) Na₂O (0.9~5.0) Al₂O₃ (1.5~7) P₂O₅ (0.9~10) M₁_xO_y (0.5~2) M₂_mO_n (82~92) SiO₂.
3. The molecular sieve according to claim 1 or 2 wherein said M₁ is Fe and
15 M₂ is Zn.
4. The molecular sieve according to claim 1 or 2 wherein said M₁ is Fe and
M₂ is Mn.
5. The molecular sieve according to claim 1 or 2 wherein said M₁ is Fe and
M₂ is Ga.
- 20 6. The molecular sieve according to claim 1 or 2 wherein said M₁ is Fe and
M₂ is Sn.
7. The molecular sieve according to claim 1 or 2 wherein said M₁ is Co and
M₂ is Mn.
8. The molecular sieve according to claim 1 or 2 wherein said M₁ is Ni and
25 M₂ is Mn.
9. The molecular sieve of claim 1 which is ZSM-5 molecular sieve.
10. Use of the molecular sieve of any one of claims 1~9 as a shape-selective
active component in catalysts or additives for catalytic cracking of petroleum
hydrocarbons.
- 30 11. A process for preparing a phosphorus- and metal components-containing
MFI-structured molecular sieve according to any one of claims 1 to 9,
characterized by the steps of:

ion-exchanging the Na-type molecular sieve having a MFI structure in a weight ratio of molecular sieve : ammonium salt : H₂O=1 : (0.1~1) : (5~10) at a temperature from room temperature to 100°C for 0.3~1 hours;

filtering;

5 introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve, wherein M1 is one of metals selected from the group consisting of Fe, Co, Ni, and M2 is one of metals selected from the group consisting of Zn, Mn, Ga and Sn; and calcining at 400~800°C for 0.5~8 hrs.

10 12. A process according to claim 11 wherein said calcining step is carried out under a water vapor atmosphere.

13. A process according to claim 11 wherein said modification is carried out by impregnating or ion-exchanging.

14. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the resultant slurry, calcining the dried solid at 400~800°C, then mixing homogeneously the calcined solid with an aqueous solution having a calculated amount of a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture.

15. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the resultant slurry, calcining the dried solid at 400~800°C, then mixing homogeneously the calcined solid with an aqueous solution having a calculated amount of a compound containing metal M1 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture; calcining the dried solid at 400~800°C, finally mixing homogeneously the calcined solid with an

aqueous solution having a calculated amount of a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

5 16. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the
10 resultant slurry, then mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

15 17. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the
20 resultant slurry, then mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M1 at a temperature from room temperature to 95°C, and oven-drying the resultant mixture; and finally mixing homogeneously it with an aqueous solution having a calculated amount of a compound containing metal M2 at a temperature from room temperature to
25 95°C, and oven-drying the resultant mixture, wherein the two metal components to be supported may be also added in a reversed sequence.

18. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously the ammonium-exchanged filter cake with
30 an aqueous solution having a calculated amount of a phosphorus-containing compound, a compound containing metal M1 and a compound containing metal M2 at a temperature from room temperature to 95°C, and oven-drying the

resultant slurry.

19. A process according to claim 13 wherein said step of introducing phosphorus, transition metals M1 and M2 to modify the molecular sieve is carried out by stirring homogeneously said ammonium-exchanged filter cake with 5 an aqueous solution having a calculated amount of a phosphorus-containing compound at a temperature from room temperature to 95°C, oven-drying the resultant slurry, calcining the dried solid at 400~800°C, and after mixing homogeneously the calcined solid with an aqueous solution having a calculated amount of a compound containing metal M1 and a compound containing metal 10 M2 in a solid : liquid ratio of 1 : (5 ~ 20), stirring the resultant mixture at 80~95°C and pH 4~7 for 2~3 hours, and then filtering the mixture, wherein the ion-exchange may be repeated for many times, and the exchanged sample may be washed with water for many times before oven-drying the washed sample.

20. A process according to any one of claims 14 to 19 wherein said 15 phosphorus-containing compound is one selected from the group consisting of phosphoric acid, ammonium hydrogen phosphate, ammonium dihydrogen phosphate or ammonium phosphate or a mixture thereof.

21. A process according to any one of claims 14 to 19 wherein said compound containing metal M1 and said compound containing metal M2 are 20 selected from their water soluble salts.

22. A process according to claim 21 wherein said water soluble salts are one selected from the group consisting of sulfate, nitrate and chloride salt.